

**REDUCTION OF ORGANIC COMPOUNDS CONTENT
OF THE WASTEWATER MILK INDUSTRY
USING COMPOSITE PERMSELECTIVE MATERIALS**

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Abstract

The wastewater results from different foods industry are generally characterized by a high organic load, far above limits discharge referred to legislation. In particular the wastewater results from different technological phases of milk industry processing, contain high quantities of organic compounds, especially proteins (caseine, β -lactoglobuline, α -lactalbumine, serumalbumine, immunoglobuline), lipide (mono, di and triacilglicerides, free fat acids, phospholipids) and disaccharides class (especially lactose).

In the treatment processes, the membrane techniques – microfiltration, ultrafiltration, reverse osmosis – are frequently used for their advantages: are continuous processes, the energetic consumption is very low, not implies temperature and phase changes, not uses chemicals adjuvant, occur in modular equipment.

The paper presents the experimental results obtained in the ultrafiltration process of a wastewater from milk industry processing- washing the reactors from production of yoghurt.

The aim of the experiments was to study the correlation between the membrane characteristics and the reduction of the organic compounds from the wastewater. 2 composite ultrafiltration membranes were used, polysulphone-polyaniline types, different by monomer used on polycondensation chemical reaction in porous structure of the base polymer.

The experimental setup that has been used was the KMS Laboratory Cell CF-1 (Koch-Membrane - Germany) ensuring a tangential flow mode in separated process.

The following indicators were analyzed from the water samples (the feed wastewater, the permeate and the concentrate): TOC, BOD, COD, total nitrogen, protein contents, conductivity. In the same time were studied the hydrodynamic, electroconductive and structural characteristics of the membranes.

Relevant in these experiments were:

- reduction the protein contents in permeate to 42%
- higher reduction of the DOC contents in permeate to 92%

The BOD/COD ratio in the permeate samples was above 0,3, which indicates the remanent biodegradable characteristics. In this case it is possible to introduce the water on the biological treatment setup improving their performances.

Keywords: proteins, membrane processes, composite membranes PSF-PANI.

Introduction

Pollution is currently one of the main problems of humanity. The environment is deteriorating step by step, the ecological systems can not adapt it to anthropic pressure factors, ecosystem self regulation is no longer possible.

In this context, there is a globally special interest developing techniques of the control and prevention of environmental pollution. The concern is the implementation of environmentally friendly technology processes, modernizing existent technologies, adoption of efficient separation process which to be achieved significant removal of pollutants and recovery, recycling of valuable compounds.

The research in the field of protection water quality demonstrated that treatment processes provide great opportunities of membrane techniques to solve this problem. The membrane techniques are frequently used for their advantages: are continuous processes, the energetic consumption is very low, not implies temperature and phase changes, not uses chemicals adjuvant, occur in modular equipment.

Industrial activities are generating wastewater effluent characterized by a significant and diverse pollution.

Wastewaters from various branches of food industry are generally characterized by a high organic loading, well above the limits provided in specific legislation.

For example the wastewater from the milk industry contains large amounts of organic compounds from the class of proteins, lipids, disaccharides.

Experimental part

The aim of the experiments were to emphasizing the ultrafiltration process performance using polysulfone – polyaniline composite membranes for separation of the organic compounds such as proteins from the wastewater generated to the milk industry.

Materials

- Polysulfone (Aldrich) M= 22000 Da;
- Aniline (Merck) ;
- 3 amino benzoic acid (Aldrich);
- N-methylpyrrolidone (Merck);
- Ammonium peroxodisulphate (Merck);
- Chlorhidric acid 37%, (Merck);
- Distilled water;
- Non woven polyester fabric type FO 2413.

Experimental conditions

- *Composite membranes obtained by phase inversion, new immersion-precipitation technique with chemical reaction:*
 - Preparation from the base polymer solution – concentration level of the PSf 10%;
 - Solvents: NMP+Aniline; NMP + Substitute aniline –3 aminobenzoic acid;
 - The coagulation solution: distilled water ;
 - Skinning polymer solutions on a textile backing into a pilot plant in continuous flux and polycondensation in oxidant mixtures (Ammonium peroxodisulphate + Chlorhidric acid)
- *Liquid testing:* wastewater from milk industry processing- washing the reactors from production of yoghurt.
- *Carrying out of protein separation experiments* - the experimental setup type KMS Laboratory Cell CF-1 (Koch-Membrane - Germania), ensuring a tangential flow mode in separated process; work pressure: 2, 4, 6 bar.



Results and discussions

In experimental conditions submitted were prepared 2 composite membranes which have the same polymer in his base structure and 2 different type of monomer (aniline/substituted aniline) used in the policondensation chemical reaction:

- Membrane M1 – obtained from polysulfone and polyaniline (PSf-PANI)
- Membrane M2 – obtained from polysulfone and substituted polyaniline (PSf-3ABA)

The two composite membranes were used to remove organic load respectively separation of proteins from a wastewater were provided by the dairy industry - washing the reactors from production of yoghurt.

Table 1 contains the experimental results obtained when was used the composite membrane PSf-PANI and Table 2 the experimental results obtained when was used the composite membrane PSf-3ABA (hydrodynamic and electroconductive characteristics) .

The water flux is determined using the equation (1):

$$J = \frac{V}{S \cdot t} \quad (\text{L/m}^2 \cdot \text{h}) \quad (1)$$

where: J = the flux ($\text{L/m}^2 \cdot \text{h}$)

V = the permeate volume (L)

S = the membrane effective area (m^2)

t = the time necessary for V liters of permeate to be collected (h)

The electroconductive characteristics are determined by measuring the conductivities of the solution food, permeates and concentrates using CONSORT C 535 multiparameter.

Table 1. The hydrodynamic and electroconductive obtained when was used the composite membrane PSf-PANI; $\sigma_i = 2,58\text{mS/cm}$ si $\sigma_c = 3,34\text{mS/cm}$

Type of membrane	P (bar)	J (l/m ² xh)	σ_p (mS/cm)
PSf-PANI	2	26	2,28
	4	53	2,33
	6	85	2,56

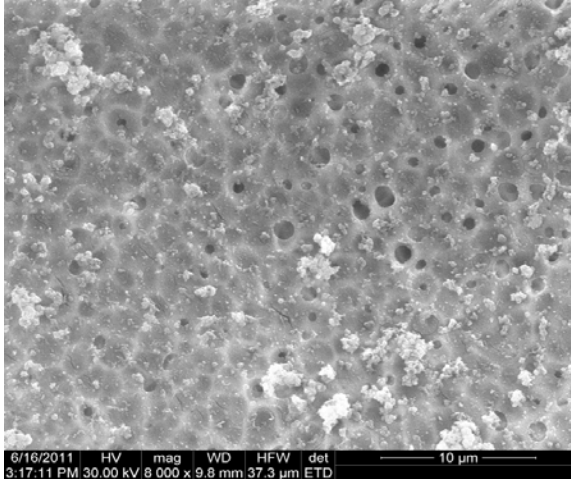
Table 2. The hydrodynamic and electroconductive obtained when was used the composite membrane (PSf-3ABA) ; $\sigma_i = 2,58\text{mS/cm}$ si $\sigma_c = 3,67\text{mS/cm}$

Type of membrane	P (bar)	J (l/m ² xh)	σ_p (mS/cm)
PSf-3ABA	2	186	2,67
	4	245	2,73
	6	198	2,81

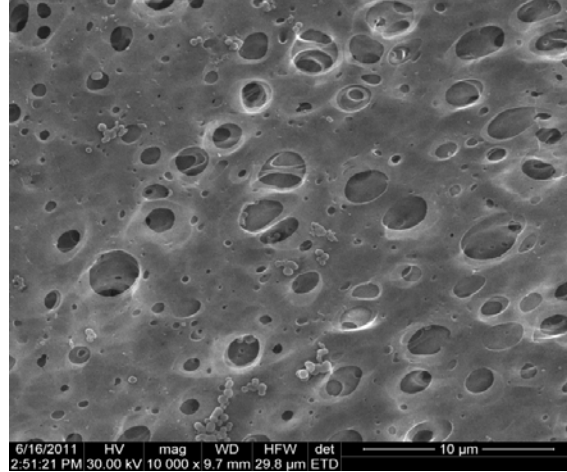
The structural characteristics of the composite membranes have been studied by scanning electron microscope (SEM), using a Field Emission - SEM Hitachi S 4500.

SEM images for the composites obtained are presented in Fig. 1 (for the composite membrane PSf-PANI) and Fig. 2 (for the composite membrane PSf-3ABA). These images allow visualizing the porous and asymmetric structure of the composite material surface. Images shows the retention of the protein by both composite membranes, too.

**Fig.1 SEM – composite membrane
 PSf-PANI**



**Fig.2. SEM – composite membrane
 PSf-3ABA**



The experimental data of the variation to main indicators quality in terms of organic load and total nitrogen content for wastewater processed through composite membranes (initial permeate, concentrate) are presented in table 3

Table 3. The main characteristics for wastewater processed through composite membranes (initial permeate, concentrate)

Sample	Characteristics				
	Proteine conc. (mg/l)	COD (mgO ₂ /l)	BOD (mgO ₂ /l)	TOC (mg/l)	Nt (mg/l)
Initial	266	4410	1460	656,5	115,1
M1permeate	157	341	105	358,2	69,54
M1concentrate	918	17125	5179	1311,1	159,3
M2permeate	189	462	148	376,5	72,83
M2concentrate	769	15814	4745	1248,5	157,3

Conclusions:

- Both types of membrane leading to retention the proteins on surface and within their microporous structure; this aspect can be viewed in SEM images of the two composite membranes
- The decrease organic loading on permeate emphasized by lowering the values of the indicators analyzed is greater for membrane PSf-PANI than PSf-3ABA
- The organic load removal efficiency were:
COD= 92% (PSf-PANI) and 89,5%(PSf-3ABA)
BOD= 92,8% (PSf-PANI) and 89,8% (PSf-3ABA)
TOC= 45,4% (PSf-PANI) and 42,6% (PSf-3ABA)
Proteine= 41% (PSf-PANI) and 29% (PSf-3ABA)
- The BOD/COD ratio in the permeate samples was above 0,3, which indicate the remanent biodegradable characteristics; its possible to introduce the water on the biological treatment setup improving their performances

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